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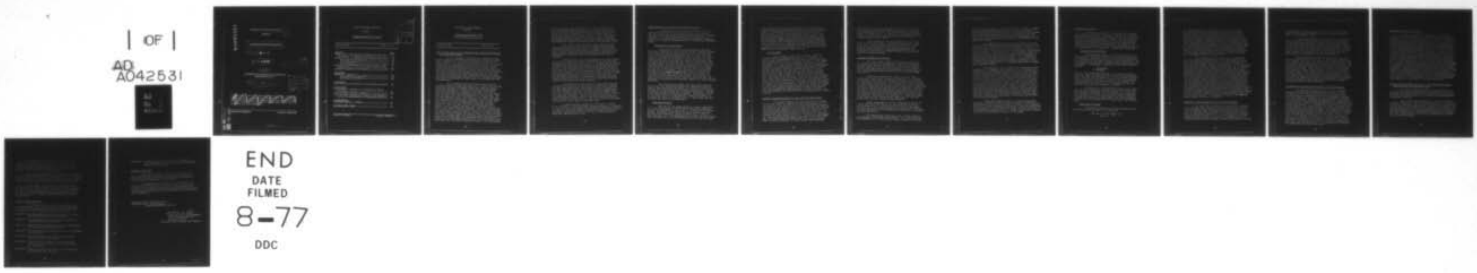

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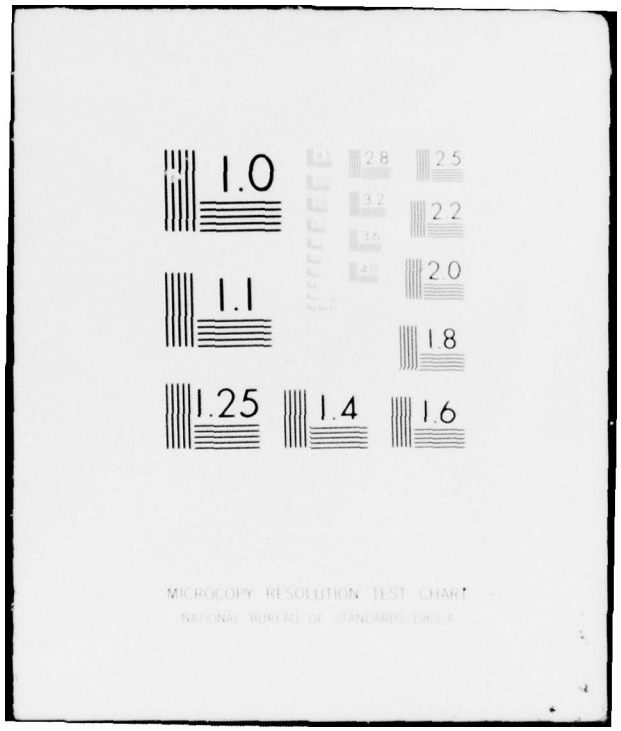
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15 March 1953 No. 7 - 6

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GROUP THEORY AND QUANTUM MECHANICS OF ELECTRON STRUCTURES IN TRANSITION METALS

Dr. K. Ganzhorn (Institute for Theoretical and Applied Physics, Stuttgart) has recently calculated electron structures in the transition metals by the aid of group theory. The specific problems with which he was concerned are a determination of the relationships between the number of d-electrons and lattice structure, and a quantum mechanical treatment of the type and magnitude of possible binding energies that might occur in these metals. His results explain the observed stability of the body-centered cubic structure for transition metals with less than seven d-electrons, and also tend to indicate why body-centered cubic metals with more than five d-electrons are ferromagnetic.

The zero-order wave functions which have the symmetry of the lattice were made up of linear combinations of atomic hydrogen-like wave functions; they are called zero-order because no interactions between neighboring atoms are considered. From the zero-order functions, Ganzhorn has made a perturbation calculation of the Bloch type to obtain the electron energies in the crystal. For the body-centered cubic (BCC) case it was found that two distinct electron types were obtained, one with the eight-fold symmetry of the nearest neighbors (type 1) and the other with the six-fold symmetry of the next-nearest neighbors (type 2); see Z.f. Naturforschung, 7a, 291, (1952). If in a transition metal one s-electron and at least three d-electrons are present, then all of these can go into the type 1 lattice functions with the body-diagonal configuration. Because there is strong overlapping of wave functions between nearest neighbors along the body diagonal, this type 1 group leads to a strongly bound band (which can contain four electrons) for electrons having antiparallel spins and to a high-lying band (which can also contain four electrons) for the case of parallel spins. The high-lying

band will not be occupied, for if it is, the BCC lattice will become unstable. Type 2 wave functions have an axial configuration; the interactions caused by the overlapping of these functions is quite small and does not contribute much to the binding energy. Type 2 wave functions also produce an upper and a lower band, the lower one containing two electrons with antiparallel spins, and the upper one containing two electrons with parallel spins.

The first transition metal which has the lower type 1 band filled is titanium with three 3d-electrons. These electrons readily go into this low-lying band, and the BCC structure is energetically favored. The spins between nearest neighbors are antiparallel so that an antiferromagnetic structure with four magnetons per atom is obtained.

Chromium with its five d-electrons is particularly interesting. The first three d-electrons go into the low lying band with the s-electron, as in titanium, and the spins of these four electrons are ordered in an antiferromagnetic manner. The fourth and fifth d-electrons assume the axial configuration of wave functions of the second type, and go into the lower band with antiparallel spins. On the average an antiferromagnetic spin structure is found for Cr with one Bohr magneton per atom, a result which is much closer to the neutron-interference measurements of the mean magnetic moment, which have given about 0.4 Bohr magneton per atom; than the predictions of older theories.

For metals with six or seven d-electrons the BCC structure is also stable, according to Ganzhorn's theory; and the theory predicts a ferromagnetic spin structure for all BCC transition metals with more than five d-electrons. This fact arises since the sixth and seventh d-electrons must go into the upper band of the type 2 functions in which the spins are parallel. Transition metals with eight or more d-electrons cannot occur in the BCC lattice structure since at least one electron per atom would occur in the high-lying band with the type 1 wave functions.

A more detailed account of this work, together with a review of the solid state research program in physics at the Institute for Theoretical and Applied Physics, Stuttgart, is given in Technical Report ONRL-8-53, available from the Technical Publications Office, Office of Naval Research, Code 250, Washington 25, D.C.

PRODUCTION OF A TAU-MESON IN A COSMIC RAY STAR

The production of a heavy meson which could be positively identified as a tau-meson has been observed for the first time in a cosmic-ray induced nuclear disintegration. The event was found and analyzed by Drs. M. Ceccarelli, N. Dallaporta, M. Merlin, G. Quareni, and G.T. Zorn, of the physics department of the University of Padova, Italy.

Description of the Event

The complete track of the tau-meson, from the point of production to the point of decay, extended through two Ilford G-5 photographic emulsions, each 1200 microns thick (with emulsions facing each other), which were exposed at an altitude of 90,000 ft. for 5½ hours at a geomagnetic latitude of 40° North. A star was found in the first emulsion, A, produced by a primary whose energy was estimated to be at least 30 Bev. The star itself had nine minimum tracks (one of which may be attributed to the primary particle, the other eight are emitted in the forward direction), three black tracks, and one grey track which was due to the tau-meson. The tau-meson was observed to be ejected in a backward direction, forming an angle of 58° with the primary. After its production in plate A, and after having traversed 7100 microns of emulsions, it came to rest in plate B after traveling 1800 microns, and underwent a characteristic co-planar decay into three charged particles.

The correlation between the heavy meson leaving plate A and the definitely identified tau-meson entering plate B was established by fixing the relative positions of plates A and B through noting in each the positon of traversing heavy primary nuclei of the cosmic radiation. The two tracks were found to correlate exactly. Furthermore, one of the light particles (presumably a π-meson) produced in the decay in plate B, entered plate A. Here again the correlation was found to be excellent.

Mass Measurements

The mass of the heavy meson in plate A, determined over its 7100 microns of track length from grain density-scattering measurements, was found to be 990 + 150 electron masses. In plate B the scattering-range method, used on the last 1800 microns of track, yielded a mass value of $890 \pm 270\ m_e$. With the correlation confirmed, one may assume that the track in B is a continuation of the track in A and

thus determine the mass by measurements on the complete track of both multiple scattering-range and grain density-range. The resultant mean of these two measurements is 955 $\pm$ 100 m_e. A more precise determination of the mass may be made from the characteristics of the decay. Its three-particle nature is indicated by the co-planarity of the secondary tracks, which is observed to be within 2°. Assuming these three secondaries to be π-mesons, together with a value of 78 $\pm$ 5 Mev for the Q of the reaction, the resultant mass of the tau-meson is found to be 975 $\pm$ 12 m_e, which is in good agreement with the mass values determined from the tau-meson track itself.

Significance

This finding is the first definite piece of evidence for the direct production of a tau-meson. It has been positively identified by means of its characteristic decay; the sign of its charge, however, is not known (as indeed the sign of all tau-mesons observed so far is unknown). It is of interest to note that the tau-meson was produced in an interaction of the primary particle (presumably a proton), not with another proton, but with a heavier nucleus in the emulsion. Based on the few tau-meson decays found so far, the guess has been hazarded that they are only produced in proton-proton collisions; this seems not to be the case. It should be noted, however, that the findings, particularly those of the Imperial College group, that tau-mesons are ejected in a backward direction holds true in this case. This may, however, be purely an effect of the probability of decay, and hence efficiency of detection, since a meson emitted in the backward direction in the laboratory system may be expected to have a much lower energy and therefore come to rest quickly. A detailed analysis of the event will be published in Il Nuovo Cimento.

CHARGED UNSTABLE PARTICLE OF MASS HEAVIER THAN PROTON

At a Royal Society Discussion Meeting in London (29 January 1953) on V-particles and heavy mesons, Dr. R. Levi-Setti of the University of Milan reported an interesting observation, made in a G-5 nuclear emulsion 400 microns thick, which was exposed to cosmic rays at high altitude. The plates were exposed without surrounding material. An unassociated particle was observed coming to rest and decaying; its track length was 11 mm. Its mass as determined by the scattering-range method was found to be about 2300 m_e. The track could be traced back into a facing plate where 5 more millimeters of track length were observed.

Dividing the total track length of 16 mm into 2 mm sections, mass values between 2100 to 2500 were obtained in the independent sections. The best mean value was 2300 ± 230. Not much can be said about the secondary particle since its track length was very short, only 120μ; its ionization was near minimum.

This represents the only example so far of an event of this mass value. No interpretation can be made as yet until more examples have been collected. It is tempting to relate this to an event suggested by the Pasadena group, namely $V^+ \longrightarrow p+\pi^o$; however, the secondary in Levi-Setti's example cannot be a proton for reasons of energy balance.

INFRARED DISPERSION OF LIQUIDS

Dr. J.H. Jaffe, Head of the Optics Division of the Weizmann Institute in Rehovoth, Israel, has recently developed some refined methods for measuring the dispersion of liquids in the infrared region with his infrared interference spectrometer. The principle of operation of this instrument has been described by him in Nature 168, 381 (1951).

These developments are likely to be of great importance in the field of chemical physics. By measuring the absolute intensities of absorption bands in the infrared spectrum, it is possible to compute oscillator strengths and transition probabilities and thereby the induced electric moments of molecules and the effective charge on the constituent atoms. Since it is very difficult to determine absolute intensities of infrared absorption bands experimentally, Dr. Jaffe has instead been measuring the optical dispersion in the infrared, which can be determined very accurately since only relative intensities are involved. It provides information which is to a large extent equivalent to that obtained from absolute intensity measurements.

Older measurements on the infrared dispersion of liquids have been carried out by the technique of prism refractometry using a hollow prism filled with the specimen, but due to the long optical path through such a prism, the above procedure is not suitable for the case of strongly absorbing materials.

The method now being used by Dr. Jaffe, based on his infrared interference spectrometer, uses a Fabry-Perot interferometer with a thin liquid sample between its plates,

which are coated with an evaporated layer of silver ~100A thick. The interferometer is crossed with a standard Perkin-Elmer prism monochrometer. The infrared light source is a stabilized carbon arc capable of supplying about 20 times the amount of light of a glowbar. An accuracy of 0.001 has been achieved by Jaffe in his measurements of the refractive index.

The method which is employed to obtain the dispersion curve consists of measuring accurately the position of fringes as a function of the wave length λ. This is done by varying the setting of the monochrometer and recording its output. The fringe pattern is produced according to the relation $2nt = m\lambda$, where n is the refractive index (a function of λ), t the separation between the Fabry-Perot plates, and m the order of the fringe. If n is constant, the fringes will appear equally spaced. However, with n varying, their separations will become non-uniform. From the fringe displacements it is therefore possible to deduce the dispersion curve.

The principal way in which this technique can be improved is to increase the sharpness of the fringes; this requires the interferometer coating to have a high reflection coefficient, but more particularly, as small as possible an absorption. The technical development work of Dr. Jaffe's group is at present concerned with improving the characteristics of the silver coating. Since it is known that the more uniform the coating is, the less absorption is produced by it; Jaffe's group is investigating various evaporation and sputtering techniques for improving the uniformity of thin (50 to 100A) silver coatings. For this purpose they have been coating collodion films which they can examine and photograph under an electron microscope. They are studying the clustering or droplet effects which occur in coating, as a function of speed of coating, and are also investigating the effect of residual gas pressure in the coating chamber.

Their technique, however, is sufficiently well developed already, to allow them to initiate a program of measurements on a series of organic liquids in the frequency region of the C-H stretching vibration. They are now calculating values of the effective charges for this vibration on the carbon and hydrogen atoms in order to gain more information on the electrostatic nature of the bond.

MOLECULAR COMPLEXES

Two types of molecular complexes have recently been investigated in the research laboratories of Royal Dutch-Shell, Amsterdam. The work, carried out by Drs. G. Schuit, J.H. van der Waals, J. Mackor, and their collaborators, dealt almost exclusively with the two types of molecular complexes best denoted as "electrostatic complexes" and as "acid-base complexes". The work on the acid-base complexes is actively in progress while that on the electrostatic complexes has largely been completed.

Electrostatic Complexes

The technique used in the investigation of the electrostatic complexes consists of the determination of the change of the solubility of picric acid in n-heptane as a function of different aromatic third components. The stability of the complexes formed between picric acid and the aromatic substances is measured by the equilibrium constant

$$K = \frac{[\text{complex}]}{[PA][Ar]} .$$

Plotting the free-energy change of the complex-forming reaction, ΔF, as obtained from the solubility measurements, against the resonance energy of the aromatic partners, a good straight line is obtained for the complexes with naphthalene, fluorene, chrysene, anthracene, and phenanthrene. The results for the benzene and for the diphenyl complexes are somewhat divergent.

In the view of the Amsterdam workers the formation of these complexes involves an electron shift from the aromatic hydrocarbon to picric acid, i.e., involves the ionization potential of the aromatic (cf. McConnell, Ham, and Platt, J. Chem. Phys. 21, 66 (1953)); thus the phenanthrene complex is more stable than the anthracene complex, although phenanthrene is less basic than anthracene.

Acid-Base Complexes

The work on acid-base complexes consists of an extensive investigation of the reaction

$$HF + Ar \rightleftharpoons [ArH]^+ + F-$$

The experimental and mathematical techniques used are similar to those of Gold, who studied the basicity of hydrocarbons in strong sulfuric acid (cf. JCS, 1952, p. 2181);distribution coefficient measurements on various aromatic substances between n-heptane and anhydrous HF are used to derive information about the equilibrium constants of interest. Although the use of anhydrous HF entails experimental difficulties, it has the advantage that by adding BF_3 or NaF respectively, the proton activity can be varied over a range of 10^9, thus making it possible to study a very wide variety of hydrocarbons. As a typical result it may be mentioned that the partition coefficient of anthracene between HF and heptane is about 20, while that of phenanthracene is about 10^{-3}.

The interpretation of the results obtained in Amsterdam differs somewhat from that given by Gold (loc. cit.) who correlated the formation of the aromatic cation with the free valence number of the aromatic system as obtained by molecular orbital calculations. It is suggested that in addition to the localization energy the ionization potential of the aromatic system will again have to be taken into account. In a microscopic sense the mechanism envisaged is that a π-electron is removed from the aromatic system and reacts with the proton to give a hydrogen atom. This is followed by the addition of the hydrogen atom to the previously created aromatic cation to provide the required product. While molecular orbital calculations on such hypothetical positively-charged aromatic radicals are not yet available, their free valence numbers may not be too different from the corresponding uncharged molecules. The preliminary correlation achieved by the Amsterdam workers consists of plotting the logarithm of the equilibrium constant of complex formation versus a suitably-weighted average of the ionization potential and the free valence number of the aromatic partner. A reasonably straight line emerges over a range in log K of 13 units.

DEFORMATION AND CLEAVAGE OF ZINC SINGLE CRYSTALS

Dr. P.L. Pratt and Mr. S.F. Pugh (AERE, Harwell) have extended their previous work on twinning and kinking on the cleavage faces of single crystals of pure zinc (J. Inst. Metals 80, 653, (1951-52)) by making observations with an opaque stop microscope of the deformation markings produced during straining. It has been observed that the crystallographic plane of cleavage is determined by the structure, and that the cracks propagate more readily in the

close-packed, slip directions. Structural imperfections such as twins, mosaic boundaries, or impurities impede or alter the cleavage process.

Twins were observed to nucleate and grow rapidly until the small applied stress was relaxed. The rate of growth, initially rapid and accompanied by audible clicks, was subsequently determined by the rate of straining and twins could be made to grow slowly without clicks. Further it was found that the boundary of a kink parallel to a twin moved to relieve the shear stress produced as the twin became thicker. The movement of the kink plane was in a direction perpendicular to the slip direction.

The investigators have identified three distinct types of deformation markings in the basal plane normal to twin traces. The first of these, an end accommodation kink, is a sharp double kink which forms at the end of a twin tip to relieve the buckling stress. The second type consists of a series of closely spaced parallel markings which appear during deformation. These markings develop in that [1010] direction most nearly perpendicular to the bending axis, and are thought to be second order kinks formed by slip on the basal plane. The third type of marking consists of long narrow ridges in a corrogated manner which are associated with the cleavage and possibly produced by the applied bending stresses in the cleaved portion of the crystal immediately after crack propagation.

THE EFFECT OF VITAMIN A ON CULTURES OF CHICK ECTODERM

Sir Edward Mellanby, G.B.E., K.C.B., formerly secretary of the Medical Research Council and an international authority on problems of nutrition and growth, is conducting an interesting series of experiments dealing with the effects of vitamin A on the development of embryo tissue in cultures. Ectoderm of seven-day old chick embryos if cultured in a medium of chick serum, can be expected to pursue a normal course of development into typical stratified squamous epithelium. If, however, vitamin A is added to the culture medium, the germinal layer of epithelium begins to produce respiratory mucous membrane. The superficial layers of squamous epithelium are sloughed off leaving a ciliated, mucous-secreting, columnar epithelium in its place. If now fresh culture medium without added vitamin A is supplied, there is a reversal of the pattern, and the respiratory epithelium is replaced with squamous epithelium. Although the mode of action of the vitamin A cannot be explained at this time, the implications of its transmutation properties are nonetheless of major importance.

HISTOCHEMICAL TEST FOR LIPASE

Dr. B.F. Martin of the Department of Anatomy, University College, Cardiff, has devised a means for better demonstrating the presence of lipase in tissue. There are three main points in his preparation: (1) the sections are not deparaffinized before incubation in the substrate (the substrate mixture used is that recommended in Methods In Medical Research, Volume 4, Section 1, G. Gomori, The Year-book Publishers, Inc., Chicago, 1951) which includes Tween 40 and a 0.05 per cent barbital buffer. When the sections are not deparaffinized, a very much stronger precipitate is obtained at the sites of lipase activity; and weaker sites of lipase activity, not demonstrated in sections deparaf-finized before incubation, are often revealed. After incu-bation the paraffin sections are dealt with in the normal way. (2) As recommended by Gomori, xylol should be avoided as a clearing agent or as a solvent for the mounting medium. The sections are taken as rapidly as possible through ascend-ing grades of alcohol to tetrachloroethylene, then through descending grades of alcohol to water. From water they are mounted in glycerine jelly. (3) Some of the sections of each series should be incubated for periods up to 48 hours so that the likelihood of missing sites of weak enzyme activity is lessened. The lipase appears as a golden brown precipi-tate, occurring in cytoplasm but never in nuclei, and with few exceptions is not seen in extracellular sites.

ANTICOAGULANT THERAPY AS AN AID TO THE RECANALIZATION OF EXPERIMENTALLY THROMBOSED ARTERIES

Dr. Helen Payling Wright of the Obstetric Unit of University College Hospital Medical School, London, has extended her previous work on the recanalization of experi-mentally thrombosed veins to the problem of experimentally thrombosed arteries.

The thrombi were produced by injecting thrombin solution (1000 units/cc) into clamped sections of the femoral arteries of rabbits. The injected substance was retained in the vessels for ten minutes before removing the clamps. The rabbits were divided into two groups; one group received no further treatment, and the second received a daily dose of 300 mg/kg body weight of "Tromexan" (a dicoumarin compound). Test for recanalization was by phlebography using diodone as the contrast medium.

The results were essentially the same as the results found in the venous studies. After three weeks the recanalization was complete in the vessels of the dicoumarin treated animals, whereas in the case of the untreated animals recanalization was in many cases not complete even after eight to sixteen weeks.

The suggested mechanism is an interference with the clotting action caused by the presence of the dicoumarin, so that no further deposition of fibrin occurs on the surface of the clot. In this situation the enzymatic digestion of the fibrin in the clot procedes without interruption.

Other studies on the size of atherosclerotic plaques in blood vessel walls indicate that the presence of dicoumarin in no way changes the size of these plaques, and leads to the conclusion that anticoagulant therapy is not effective in atherosclerosis even though of value in the recanalization of vessels thrombosed artificially by blood clots.

TECHNICAL REPORTS OF ONRL

The following reports have been forwarded to ONR, Washington, since the last issue of ESN. Copies may be obtained from the Technical Publications Office, Code 250, Office of Naval Research, Washington 25, D.C.

ONRL-2-53 "The Thermodynamic Behavior of Carbon in Liquid Iron-Chromium Alloys" by E. Epremian

ONRL-10-53 "Electron Therapy of Skin Tumors, University of Göttingen" by J.L. Tullis

ONRL-11-53 "Royal Society Discussion Meeting on V-Particles and Heavy Mesons" by S.F. Singer

ONRL-12-53 "Neutron Detecting Thermopiles in Use at Harwell" by J.K. Beling

ONRL-13-53 "Photomultiplier Tubes Made by N. Schaetti, E.T.H., Zürich" by W.L. Hyde

ONRL-15-53 "Facilities for Research in Nuclear Physics and Cosmic Rays in Argentina" by J.K. Beling and S.F. Singer

ONRL-16-53 "Physics of Solids Research at the University of Gottingen" by J.R. Reitz

ONRL-18-53 "Formal Papers Given at the Sixth Annual General Meeting of the Experimental Psychology Group" by C.H. Graham

PERSONAL NEWS ITEMS

Mr. F.R.N. Nabarro, lecturer in metallurgy at the University of Birmingham, has accepted the Chair in Physics at the University of Witwatersrand, Johannesburg The appointment commences in June, 1953.

Dr. Kerim Erim, Chairman of the Department of Mathematics, University of Istanbul, died on the 28th of December 1952. Participants in the Eighth International Congress on Theoretical and Applied Mechanics (August 1952) will remember Dr. Erim for his activities in the organizing of the Congress.

Prepared by the Scientific Staff
Submitted by Dr. S.R. Aspinall
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